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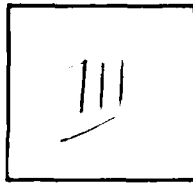


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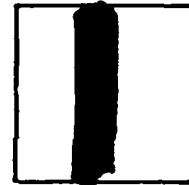
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Laser Propagation Research. Volume II

DOCUMENT IDENTIFICATION

Rpt. No. OMI-80-008(12)

Contact DAAD07-80-C-0056

Nov. 80

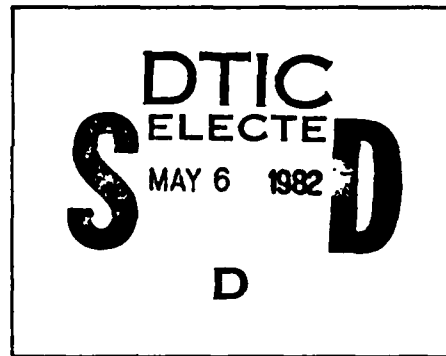
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LASER PROPAGATION RESEARCH
VOLUME II
GASEOUS AND PARTICULATE CHARACTERIZATION
OF THE ATMOSPHERE

Wayne L. Flowers

Prepared for
Atmospheric Sciences Laboratory
White Sands Missile Range, New Mexico

Contract DAAD07-80-C-0056

November 1980

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1 REPORT NUMBER	2 GOVT ACCESSION NO	3 RECIPIENT'S CATALOG NUMBER
	AD-A114 161	
4 TITLE (and Subtitle) LASER PROPAGATION RESEARCH VOLUME II GASEOUS AND PARTICULATE CHARACTERIZATION OF THE ATMOSPHERE		5 TYPE OF REPORT & PERIOD COVERED Technical Report 3/80 - 10/80
7 AUTHOR(s) Wayne L. Flowers		6 PERFORMING ORG REPORT NUMBER OMI-80-008(II)
9 PERFORMING ORGANIZATION NAME AND ADDRESS OptiMetrics, Inc. 2000 Hogback Road, Suite 3		8 CONTRACT OR GRANT NUMBER(s) DAAD07-80-C-0056
11 CONTROLLING OFFICE NAME AND ADDRESS Atmospheric Sciences Laboratory US Army Electronics R&D Command WSMR, NM 88002		10 PROGRAM ELEMENT PROJECT TASK AREA & WORK UNIT NUMBERS Volume II Task F.3.1
14 MONITORING AGENCY NAME AND ADDRESS (if different from Controlling Office)		12 REPORT DATE November 1980
		13 NUMBER OF PAGES 181
		15 SECURITY CLASS (of this report) Unclassified
		15a DECLASSIFICATION/DOWNGRADING SCHEDULE
16 DISTRIBUTION STATEMENT (of this Report)		
<div style="border: 1px solid black; padding: 5px; text-align: center;"> DISTRIBUTION STATEMENT A Approved for public release; Distribution Unlimited </div>		
17 DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18 SUPPLEMENTARY NOTES		
19 KEY WORDS (Continue on reverse side if necessary and identify by block number)		
High Energy Laser H ₂ O, HDO, N ₂ O, O ₃ , THC, CH ₄ Atmospheric Transmission Fourier Transform Spectrometer (FTS) ARKY Site NOP Site Solar Spectrum		
20 ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>An existing Fourier Transform Spectrometer (FTS) data base of slant path atmospheric transmission spectra using the sun as a source is described. Recent improvements to the FTS measurements system are discussed and results of pyroelectric radiometer measurements of slant path solar transmission are reviewed.</p> <p>Slant path atmospheric transmission modeling developments and use of these models in the interpretation of slant path FTS transmission data are discussed.</p>		

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Techniques for atmospheric absorbing gas vertical density profile extraction are presented and results of model comparisons with FTS data are reviewed.

Recent measurements of H_2O , N_2O , THC , CH_4 , O_3 , and CO_2 atmospheric concentrations at the ARKY and NOP sites at WSMR are presented and discussed. Results of aerosol particulate distribution and mass loading measurements at the WSMR-NOP sites are presented and described.

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CONTENTS

1.	INTRODUCTION.....	1
2.	ATMOSPHERIC CHARACTERIZATION MEASUREMENTS.....	2
2.1	Gas Species Measurements Data Collection Schedule.....	2
2.2	Gas Sampling Measurements at ARKY Site.....	5
2.2.1	Water Vapor Measurements at ARKY Site.....	5
2.2.2	Deuterated Water Vapor.....	7
2.2.3	Nitrous Oxide Measurements at ARKY Site.....	8
2.2.4	Methane.....	8
2.2.5	Total Hydrocarbons Measurements at ARKY Site.....	8
2.2.6	Carbon Dioxide Measurements at ARKY Site.....	9
2.2.7	Ozone Measurements at ARKY Site.....	9
2.3	Gas Sampling Measurements at NOP Site.....	11
2.3.1	Water Vapor Measurements at NOP Site.....	11
2.3.2	Nitrous Oxide Measurements at NOP Site.....	13
2.3.3	Total Hydrocarbon Measurements at NOP Site.....	13
2.3.4	Carbon Dioxide Measurements at NOP Site.....	14
2.3.5	Ozone Measurements at NOP Site.....	14
2.4	Aerosol Particulate Measurements.....	15
2.4.1	Scattering Coefficient Measurements at NOP Site.....	15
2.4.2	Aerosol Mass Concentrations Measurements at NOP Site.....	16

2.4.3	Results of Aerosol Mass Concentration Measurements at NOP Site.....	17
2.4.4	Aerosol Particle Size Distribution Instrumentation.....	17
2.5	Status of the Gas/Aerosol Van.....	18
2.6	Planned Future Efforts and Directions.....	18
3.	CONCLUSIONS AND RECOMMENDATIONS.....	20
	REFERENCES.....	24
APPENDIX A-1.	PLOTS OF MEASURED ATMOSPHERIC GAS CONCENTRATIONS - ARKY SITE.....	25
APPENDIX A-2.	PLOTS OF MEASURED ATMOSPHERIC GAS CONCENTRATIONS - NOP SITE.....	82
APPENDIX A-3.	MAXIMUM, MEAN AND MINIMUM VALUES OF MEASURED GAS CONCENTRATIONS AT NOP SITE.....	155
APPENDIX A-4.	PLOTS OF NEPHELOMETER AND AEROSOL MASS MONITOR DATA AT ARKY SITE.....	159
APPENDIX A-5.	PLOTS OF AEROSOL MASS MONITOR DATA AT THE NOP SITE.....	169

LIST OF FIGURES AND TABLES

Figure 1.	Sensor Location.....	12
Table 1.	Summary of Atmospheric Gas Data Collected at Arky Site.....	6

1
INTRODUCTION

This report describes work performed for the Atmospheric Sciences Laboratory (ASL) in support of their High Energy Laser Meteorology (HELMET) responsibility to the High Energy Laser Systems Test Facility (HELSTF). The measurements and analyses reported herein continue and extend work begun in 1977. It describes work completed during the period 1 March through 30 September 1980.

In the interest of clarity, this report has been separated into two volumes. Volume I describes progress, results, and data analyses associated with the measurements of atmospheric transmission spectra using the sun as a source. Volume II describes recent work carried out in atmospheric gas analysis studies and contains results of measurements performed during the most recent reporting period. This volume is devoted to the Gaseous and Particulate Characterization of the Atmosphere.

ATMOSPHERIC CHARACTERIZATION MEASUREMENTS

The work reported herein is a continuation of gas concentration measurements described elsewhere [1,2,3]. In those reports, detailed descriptions of the gas analyzers used to determine ambient concentrations of H_2O , HDO , N_2O , CH_4 , CO_2 , and total hydrocarbons (THC) were given, and data were presented from measurements made at High Energy Laser System Test Facility (HELSTF) sites (MAR & ARKY) between August 1977 and 31 December 1979.

In this report gas data taken between 25 March 1980 and 30 September 1980 will be presented. These data represent measurements taken at ARKY site and North Oscura Peak (NOP) during regularly scheduled runs as well as those taken subsequent to these runs.

In addition, aerosol and particulate instrumentation incorporated into the gas/aerosol van will be discussed and data obtained with this instrumentation will be presented where available.

Continuing work on gas/aerosol van instrumentation will also be discussed.

2.1 GAS SPECIES MEASUREMENTS DATA COLLECTION SCHEDULE

During the period covered in this report, atmospheric gas data were obtained at ARKY site during regularly scheduled Atmospheric Sciences Laboratory (ASL) data gathering runs on 26-27 March 1980, 3-5 June 1980, and 20-21 August 1980.

Measurement techniques were similar to those described earlier [1]. Further calibration of the MIRAN II analyzer

used to determine the effects of atmospheric carbon dioxide on the measurements was performed. From this calibration, correction factors were determined for data taken prior to the August data run. Starting with the August data run the necessary scrubbers were available and used to scrub atmospheric carbon dioxide from the air sampled by the MIRAN II analyzer in order to eliminate this interference.

All analyzers were operational for these runs with certain exceptions noted below. Although all analyzers were operational when the system was shut down in December 1979, at the start of the March 1980 data run the methane and total hydrocarbon (THC) analyzers were not operational due to an inoperative cutter* and failure of the DC power supply for the solenoid valves. One ozone analyzer was also inoperative due to mice nesting activities. A spare ozone unit was brought on line for the run while the damaged one was repaired. A new solenoid valve power supply was installed during the run, however operation of the total hydrocarbon analyzer was erratic and a spare on order was not yet available. The non-methane cutter was removed after the run for servicing, however as of this writing not all of the spare parts had been received.

During the start-up for the June data run, two of the three water vapor sensors on the 32m tower were found to be totally inoperative and the third one was erratic and failed completely after the run. The reason for the sudden failure of these units is not known but possibly the tower was hit by lightning. One spare was on hand and this was installed at the 4m level of the tower. Since the sensors are not readily field serviceable, they were returned to the manufacturer for repair. A spare non-methane cutter

* A device used to remove selectively or to purge certain gas constituents from the sample volume.

was installed; this unit, though, was found to have a faulty temperature control circuit and was returned to the manufacturer for service under warranty. Several line power failures during this data run resulted in erratic operation of the THC analyzer and data logger.

During the August data run an internal hydrocarbon leak was discovered in the flame ionization detector used with the non-methane cutter. This unit was then taken off line, thus only total hydrocarbon data are available for this run. All other analyzers were operational.

Occasionally during a scheduled data run, data would not be recorded on the HELSTF data acquisition computer due to diverse causes such as amplifier failure, broken data leads, noisy connections, etc. This was the case for some of the ozone and carbon dioxide data during the March 1980 run. The missing data were available, however, from the gas/aerosol van data logger printout. These data were entered into files on an ASL Hewlett-Packard (HP) 2835 microcomputer by hand and were plotted using this system.

Supplemental data for all gases except methane were taken during the period 6-10 June 1980. These supplemental data are available as hourly averages printed on paper tape during the experiment but they must be entered into digital files on the HP 2835 system since no magnetic tape recording facilities were available during the data collection period. Those data which are available in plotted output format are presented in Appendix A.

Supplementary data for the period between the end of June through 30 September 1980 are not available because of data logger memory failure. The logger was sent back to the manufacturer for modification.

A summary of available ARKY data is given in Table 1.

Gas sampling data were also obtained at NOP during the period 16-28 April 1980. All data during this run were sampled at a height of 4m at the location of the van. Water vapor, nitrous oxide, carbon dioxide, and ozone data are available as half-hour averages for nearly the entire period. Total hydrocarbon data were collected, after modifications to the gas handling system were completed, during the period 22-24 April 1980 until the fuel gas supply for this analyzer was depleted.

Data obtained at ARKY site using the HELSTF data acquisition system are reduced and plotted by ASL, using data reduction routines provided by OMI. To date, data collected during the periods 26-27 March 1980 and 3-5 June 1980 are available in plot format. Data from ARKY site are available only as data logger printouts and all NOP data have been reduced and plotted by OMI. To date data for the periods 25-26 March 1980, 3-5 June 1980 and a partial data set for the period 6-10 June 1980 collected at ARKY site are available in plotted form. All NOP data are available as plots. The available plots are reproduced in Appendix A.

The data for individual gas species are discussed in separate sub-sections below. Daily plots of data collected at ARKY site are presented in Appendix A-1, daily plots corresponding to data collected at NOP site are presented in Appendix A-2, while average, maximum and minimum values of the NOP site data are presented in Appendix A-3. Time of day in what follows means Mountain Standard Time (MST), whether stated as hours or MST.

2.2 GAS SAMPLING MEASUREMENTS AT ARKY SITE

2.2.1 WATER VAPOR MEASUREMENTS AT ARKY SITE

The most pronounced diurnal variation in water vapor concentration occurring on 26 March 1980 was observed at

TABLE 1. SUMMARY OF ATMOSPHERIC GAS DATA
COLLECTED AT ARKY SITE

(5 March 1980 - 30 September 1980)

GAS	LOCATION	HEIGHT (m AGL)	DATA
H ₂ O, HDO*	Met Tower	2	26,27 March 1980
	Met Tower	2	20,21 August 1980
	Met Tower	4	26,27 March 1980
	Met Tower	4	2-10 June 1980
	Met Tower	4	
	Met Tower	32	26,27 March 1980
	Met Tower	32	20,21 August 1980
N ₂ O	Met Tower	4	26,27 March 1980
	Met Tower	32	2-10 June 1980
	Met Tower	32	20,21 August 1980
CH ₄	No Data		
THC	Met Tower	4	3,4,5 June 1980
	Met Tower	32	20,21 August 1980
CO ₂	Met Tower	4	26,27 March 1980
			2-10 June 1980
			20,21 August 1980
	Met Tower	32	26-27 March 1980
			2-10 June 1980
			20,21 August 1980
O ₃	Met Tower	4	26,27 March 1980
			2-10 June 1980
			20,21 August 1980
	Gas/Aerosol Van	4	26,27 March 1980
			2-10 June 1980
			20,21 August 1980

* Derived from H₂O Data using adjusted abundance ratio
of HDO/H₂O

the 2m level of the met tower. Here a sharp minimum in concentration as a function of time of ≈ 2.6 torr was observed around 0600 MST while a broad concentration maximum occurred between 0900 and 1800 hours during which time the concentration was greater than 4 torr. Another sharp minimum value (3 torr) occurred briefly around 2000. The general pattern at 4m was similar; in fact, it virtually overlaps the 2m pattern between 0000 and 0800 MST and between 2030 and 2400 MST. The daytime values at 4m however are about 1-1/2 torr lower than the values at 2m and are much closer to the 32m values between 1200 and 1800 MST. The pattern at 32m exhibits much less variability than the pattern at 2m and 4m, varying only between 2.0 and 2.8 torr with less pronounced maximum and minimum values, although a general relationship to the lower level data can be seen in Figure A-1.1.

On 27 March 1980 identical patterns are seen at the 2m, 4m, and 32m levels with the 32m values being about 1 torr less than the 2m and 4m values. The vapor pressure gradually rises from 0000 MST to 1400 MST. At 1530 MST there is a sudden increase in vapor pressure by $\approx 60\%$ corresponding to a period of marked variation in wind direction followed by a gradual decrease to the values before the spike increase.

On 3 June 1980 vapor pressure started out quite low ($\approx 1-1/2$ torr) but a marked jump to 6 torr occurred between 0900 and 1100 MST followed by a gradual decline, with occasional large excursions (± 0.8 torr), to 2.3 torr at 2400 MST on 4 June 1980.

2.2.2 DEUTERATED WATER VAPOR

No direct measurements of HDO concentration were made during this period, the values reported were obtained from

the water vapor measurements using a modified canonical value for the abundance of HDO relative to H₂O [4,5].

2.2.3 NITROUS OXIDE MEASUREMENTS AT ARKY SITE

Nitrous oxide measurements were taken at the 32m level of the 32m met tower starting with the June 1980 data run.

Nitrous oxide concentrations were characterized by nearly constant values throughout a day with little or no diurnal pattern. Concentrations varied between 0.33 and 0.35 ppm on the third and fourth of June, dropping to 0.3 ppm by 2400 MST on the fifth of June. There was a further decrease to ≈ 0.28 ppm by 2400 MST on the sixth of June. From then until data acquisition stopped on the tenth of June, concentrations averaged 0.28 ppm with little variation. The minimum value seen between the 6 June and 10 June data was 0.27 ppm at 2400 hours on the ninth of June. Small increases occurred around 0800 hours on 7 and 9 June, to a value of 0.315 ppm (7 June) and 0.295 ppm (9 June). At the present time there are insufficient data to determine whether or not a diurnal change in nitrous oxide concentration occurs.

2.2.4 METHANE

No methane data were collected due to failure of the non-methane cutter.

2.2.5 TOTAL HYDROCARBONS MEASUREMENTS AT ARKY SITE

Total hydrocarbon data are only available for 4 and 5 June 1980. Measured THC concentrations were quite low (<1.4 ppm) with no discernable diurnal pattern and are probably nearly all methane.

2.2.6 CARBON DIOXIDE MEASUREMENTS AT ARKY SITE

No consistent diurnal pattern was present on 25-27 March 1980. Measured concentrations on 25 March ranged from a low of 287 ppm at the 32m level at 2330 hours to a maximum of 352 ppm at the 4m level at 1530 hours. Observed concentrations of 25 March were widely varying, whereas on 27 March they were fairly uniform, averaging ≈ 322 ppm. On 25 and 26 March the 4m values were lower than the 32m values, with the exception of a few hours on 25 March rather than just during daylight hours as would normally be the case. On 27 March the reverse situation occurred during that period of time for which data from both levels are available. The 32m values are larger than the 4m values by about 2 ppm indicating CO_2 depletion near the ground. The usual mechanism for this effect is plant photosynthesis; the pattern usually reverses during the evening hours when respiration takes place.

Carbon dioxide concentrations at both the 4m and 32m level show a characteristic decrease in the morning hours near sunrise (0500-0800 hours) on 3, 4, and 5 June 1980. This behavior could be due to a sudden spurt of photosynthetic activity probably inhibited by the intense heat and sunlight later in the day when concentrations rise again. Mid-day decreases are seen at the 32m level on 4 and 5 June with little to no increase at the same time in the 4m values. It is undetermined at this time whether or not this effect is due to a positive CO_2 flux corresponding to photosynthetic activity or net transport of CO_2 out of the region.

2.2.7 OZONE MEASUREMENTS AT ARKY SITE

Much of the ozone data collected during 25-28 March 1980 show no discernible temporal pattern. However, on

26 March a minimum occurs in the O_3 concentrations measured both at the van and the tower locations between 0400 and 0800 hours and again between 2000 and 2400 hours. The minimum occurring during 0400-0800 hours is seen at the tower but not at the van. Another decrease is also seen between 1430 and 1630 hours at the tower. The absolute values of the measured concentrations were quite low, less than 50 ppb at the van location and <40 ppb at the tower.

On 3 June 1980, measured O_3 concentrations at the 4m level of the met tower were less than 30 ppb during the entire day and exhibited a broad decrease occurring between 0300 and 0900 hours, wherein the concentrations dropped to a minimum value of 10 ppb. The depression of O_3 concentration values was barely noticable at the van intake. Concentrations at the van were more variable but only exceeded 40 ppb during a brief period (2100-2200 MST); the remainder of the time, measured values varied between 20 and 40 ppb.

Concentrations measured at the tower on 4 and 5 June exhibited a similar pattern with a sharp drop in concentration of 15 ppb or more occurring between 0000 and 0200 hours followed by a gradual increase throughout the day to the levels observed (\approx 30 ppb) before the early morning drop. This pattern was somewhat different from that observed at the van.

Ozone concentrations measured at the 4m level of the gas/aerosol van between 4 and 10 June 1980 exhibit a definite diurnal pattern with low values (\sim 20-30 ppb) occurring in the late evening - early morning hours, generally between 2000 hours and 1000 the next day, followed by high concentrations (\sim 30-40 ppb) during the afternoon and early evening hours.

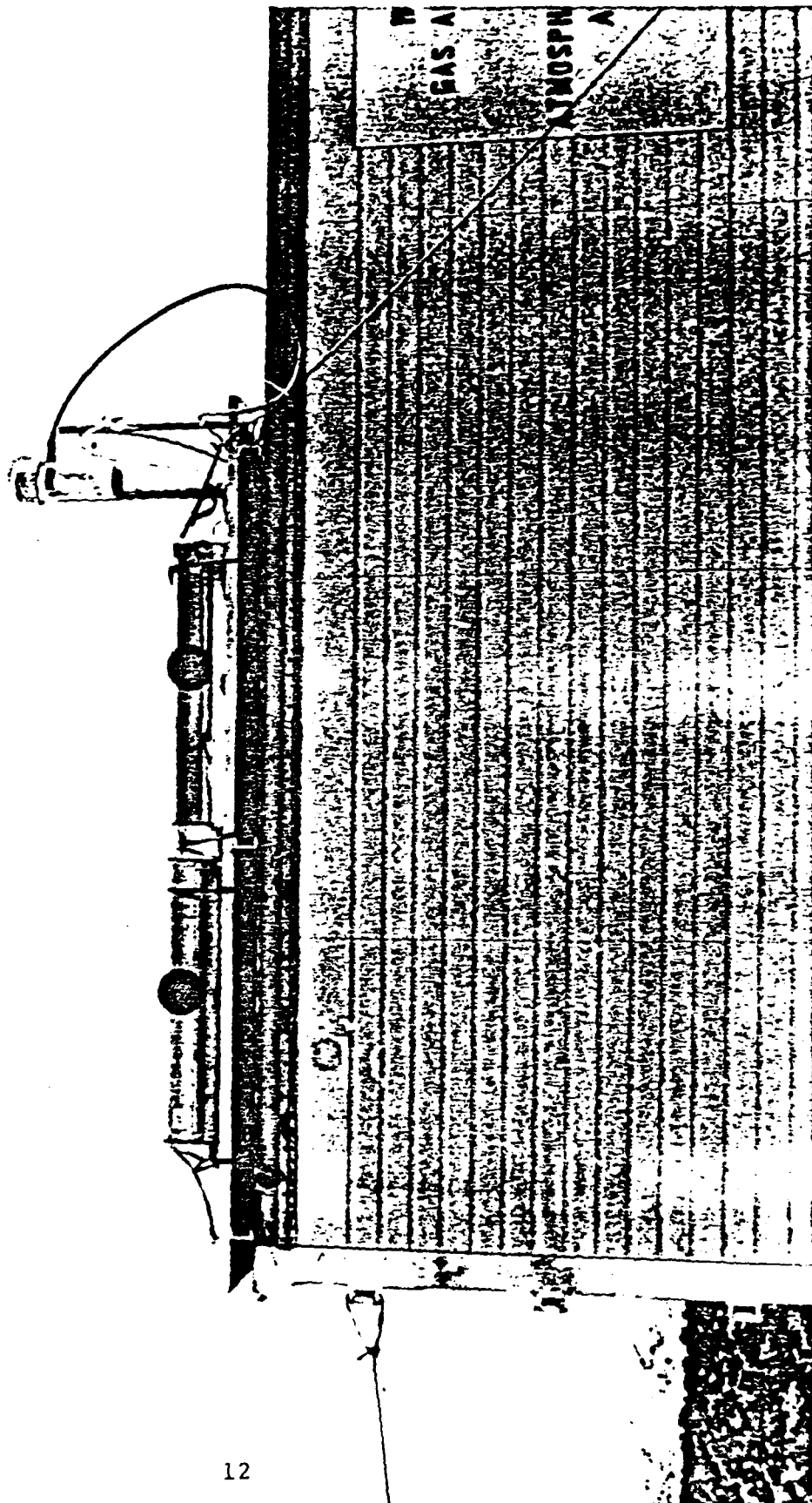
2.3 GAS SAMPLING MEASUREMENTS AT NOP SITE

Atmospheric gas concentration data were collected at NOP site for water vapor, nitrous oxide, carbon dioxide, and ozone between 10 April and 28 April 1980. Total hydrocarbon data were taken between 22 and 24 April 1980. All data were collected at 4m above ground level (AGL) at the gas/aerosol van (see Figure 1) with the van located at an elevation estimated to be 2435 - 2400m above sea level (ASL). The majority of the data were recorded in half-hour averages.

2.3.1 WATER VAPOR MEASUREMENTS AT NOP SITE

Measured water vapor partial pressure remained less than 1.7 torr between the start of the run at 1800 MST on 10 April and 1600 MST on 11 April. An increase of a factor of two (to 3.3 torr) occurred over the next three hours as slightly moister air moved into the site. A gradual decrease in water vapor pressure then occurred but the partial pressure stayed between 2 and 3 torr until 0800 on 14 April when another influx of moisture raised the H₂O partial pressure from 2.2 torr at 0800 MST to 3.3 torr at 1300 MST. A sharp decline in vapor pressure then occurred from 3.0 torr at 1500 to 1.6 torr at 1900 MST. The partial pressure then remained between 1.5 torr and 2.5 torr between 1900 MST on 14 April and 1500 MST on 16 April. A six-hour period of low concentrations was then observed (between 1600 and 2200 MST) with measured values falling between 0.6 to 1 torr. The lowest water vapor reading seen during the run was 0.6 torr, occurring at 1830 MST on 16 April 1980.

A sharp increase (0.8 torr to 2.8 torr) occurred between 2200 and 2230 MST on 16 April as a moisture cell rapidly moved into the area of the NOP site. The vapor



pressure gradually dropped and remained between 1 and 2 torr for the remainder of the period between 1600 MST on 17 April and 0200 on 21 April.

A regime of much moister air then moved in raising the water vapor concentration from 2 torr at 0200 MST to 5 torr by 0500 MST. Concentrations stayed above 4 torr after 1200 MST on 22 April; the maximum observed value of 6.9 torr was recorded at 1430 MST on 21 April 1980.

After 1200 MST on 22 April a somewhat drier regime with large concentration fluctuations prevailed until the end of the run. Between 1200 MST on 22 April and 1200 MST on 28 April concentrations varied between 1.5 torr and 3.5 torr with the lower values occurring predominantly between 1600 MST on 23 April and 0300 on 24 April.

2.3.2 NITROUS OXIDE MEASUREMENTS AT NOP SITE

Nitrous oxide concentrations measured during the run are characterized by a distinct diurnal pattern of a broad early morning maximum centered about 0800 MST followed by a broad early evening minimum centered near 1900 MST. An anomalous sharp increase was seen early in the morning of 12 April around 0400 MST. This may just be an artifact but there were no known instrumentation malfunctions at the time. Excluding the anomalous high value the range of observed concentrations was 0.26 to 0.39 ppm with an average value of 0.31 ppm during this run.

2.3.3 TOTAL HYDROCARBON MEASUREMENTS AT NOP SITE

When attempts were made to operate the hydrocarbon analyzers at the NOP site, they could not be ignited due to changes in air-fuel mixture requirements at the reduced atmospheric pressure of the NOP site. Changes in air and

fuel capillaries in the instruments were then made for altitude compensation. These changes proved successful and 47 hours of data were acquired between 22 and 24 April before fuel gas supplies were expended. No diurnal pattern was observed in these data; peak concentrations were measured shortly after the measurements began with concentration values around 1.2 ppm recorded in the early hours of 22 April. A decline to 0.92 ppm by 2400 MST then occurred. An undulating decline to 0.8 ppm occurred throughout the day during 23 April followed by a gradual rise to 0.87 ppm by the time measurements ended on the 24th. The measured hydrocarbon concentrations are assumed to be due to background methane.

2.3.4 CARBON DIOXIDE MEASUREMENTS AT NOP SITE

Carbon dioxide concentrations ranged between 340 and 390 ppm during the course of the run with the average concentration being ≈ 360 ppm. A pronounced diurnal pattern occurred, consisting of a broad early morning maximum usually peaking around 0700 MST followed by a broad late afternoon minimum usually reaching the lowest levels around 1700 MST. This pattern is consistent with the usual photosynthetic and respiratory activities. Normally maximum to minimum differences on the order of 20 ppm are observed.

2.3.5 OZONE MEASUREMENTS AT NOP SITE

Ozone levels were highly variable throughout the run with no particular pattern. Levels were fairly low, varying between 5 ppb and 50 ppb with an average concentration of slightly over 30 ppb.

2.4 AEROSOL PARTICULATE MEASUREMENTS

Starting with the April 1980 run at NOP three point sampling aerosol particulate analyzers were incorporated in the gas aerosol van to obtain information on scattering coefficient, total mass loading and aerosol size distribution. No data were gathered as to type of particulate. Brief descriptions of the analyzers follow. The majority of the data are plotted by ASL. Plots available to date are presented in Appendix A-4.

2.4.1 SCATTERING COEFFICIENT MEASUREMENTS AT NOT SITE

Scattering coefficient is determined by a Meteorology Research Inc. integrating nephelometer and recorder (Model 1550B and System 2050B). This analyzer is intended to make objective and reproducible measurements of the visual quality of the sampled air. This is done by measurement of the atmospheric extinction coefficient due to backscattering by suspended particulate matter in the sample air.

This analyzer utilizes a UV filtered Xenon flashlamp as a light source to make its response closer to that of the human eye. The volume sample of air is defined by a series of diaphragms, there being no mirrors or lenses used in the optical train. A reference phototube is used for monitoring the flashtube directly and to provide a signal used for backing out residual background signals due to stray light in the optical assembly. The instrument output is displayed in units of scattering coefficient (10^{-4} m^{-1}), meteorological range, or mass concentration using an approximate canonical conversion factor. Measurements with this instrument are made at the 4m level at the gas/aerosol van.

Internal calibration is provided by either sampling filtered air during a normal measurement or by viewing an

internal light trap. For "absolute" calibration, clean freon is used as a standard aerosol source.

Data are recorded using a strip chart and are plotted by ASL personnel as mass concentration.

The experience gained to date with this system during three ARKY site and one NOP site data runs indicates a moderate to severe drift problem with the instrument which should be corrected to avoid extensive loss of data gathering time on account of the need for frequent calibration.

2.4.2 AEROSOL MASS CONCENTRATION MEASUREMENTS AT NOP SITE

Mass concentration is determined by a GCA Corporation Aerosol Mass Monitor (Model APM, 6000 Series). This analyzer draws in sample air through a venturi orifice at a constant rate, then collects particles in the air on a fiberglass reinforced filter tape for measurement of the collected mass by beta-ray attenuation. An electronic subsystem performs signal conditioning, beta-count logging, mass concentration measurement and control of the various mechanical operations. Data are presented in a hard copy 'data logger' format. This unit utilizes long sampling times for decreasing measurement error. Typical times used during data runs are 60 or 120 minutes. Data reduction and plotting have been done by both ASL and OMI personnel.

The experience gained to date with this system during three ARKY site and one NOP site data runs indicates a severe zero stability problem, the effect of which on the measured data is as yet unknown. An additional problem with the use of this instrumentation arises because, during the ARKY site runs, the measured mass concentrations were near or below the nominal advertised minimum measurement capability of the unit.

2.4.3 RESULTS OF AEROSOL MASS CONCENTRATION MEASUREMENTS AT NOP SITE

Aerosol mass concentrations measured on 26 and 27 March 1980 and 3 and 4 June 1980 were less than $45 \mu\text{gm}/\text{m}^3$ whether measured both with the mass monitor or the integrating nephelometer. No diurnal pattern was observed; in fact, maxima in the nephelometer data frequently corresponded to minima in the mass monitor data. Examples of such correspondences occurred at 2200 MST on 27 March 1980, and at 1100 and 2200 MST on 4 June 1980. These results demonstrated the difficulty of making measurements at the very low particulate concentration values encountered which are at the limit of the instrumentation measurement sensitivity.

2.4.4 AEROSOL PARTICLE SIZE DISTRIBUTION INSTRUMENTATION

Particulate sizing is done with a Particle Measuring Systems, Inc. "Classical Scattering Aerosol Spectrometer Probe" and associated data acquisition system (Models CSASP-100 and DAS-64). This unit sizes particles by their forward scattering of He-Ne laser light at 6328\AA . Four independent size ranges are provided with fifteen size classes within each range. The nominal useful total range is 0.3 to 20 micron diameter particles, thus eliminating such particulates as pollen from consideration. The system installed in the gas/aerosol van contains and incorporates data processing electronics and a tape recorder. Consequently the HELSTF computer and recording facilities are not used in conjunction with the aerosol distribution measurements. Data are reduced and plotted as absorption and/or extinction coefficient by ASL.

2.5 STATUS OF THE GAS/AEROSOL VAN

The basic instrumentation installation in the gas/aerosol van has been completed. The work remaining to be done is the installation of peripheral items including a receiving telescope for the HDO-GFCS, improved particulate sensor intakes, final installation of calibration gas sampling lines, rewiring of some data leads and conversion of analog data output format to serial digital format plus the repair of currently out-of-service equipment. Equipment currently awaiting service parts include: one ozone analyzer; the data logger; one non-methane cutter; one flame ionization detector; a sample pump; and the strip chart recorders.

2.6 PLANNED FUTURE EFFORTS AND DIRECTIONS

In addition to the gas/aerosol van instrument modifications and servicing mentioned above, future efforts will include further investigation of the drift problems associated with the integrating nephelometer and mass monitor, incorporation of a minicomputer and tape recorder in the gas/aerosol van to enhance its stand-alone capability, and incorporation of atmospheric molecular absorption models in the real-time HELMET laser extinction prediction display. Data from different sampling heights are now available so that development of mass flow models for carbon dioxide and water vapor can be initiated.

Up to the present time deuterated water vapor has been determined by the application of the best estimate of the canonical value of the ratio of HDO/H₂O along with measured water vapor data. It is recommended that further effort be expended in confirming this estimate, possibly at the expense of some of the monitoring efforts for which a good data base has already been established. Two approaches

should be undertaken simultaneously; one method is the determination of the D/H ratio for "grab samples" using mass spectrometric determination, the other is by use of long path optical methods. The latter requires the expense and effort associated with the procurement of the necessary ancillary equipment such as transmitting and receiving telescopes and lock-in amplifiers needed to bring the HDO-GFCS into operational status; the other long-path optical method would use the ASL Carson-Alexiou Fourier Transform Spectrometer (FTS) at the HELSTF site in either the solar source or long path horizontal transmission mode for the measurement.

The "grab sample" method is potentially the easiest and cheapest to implement if the ARMTE Chemistry Laboratory facilities can be made available for the mass spectrometric determinations.

3
CONCLUSIONS AND RECOMMENDATIONS

During the three prescribed data collection periods, namely 26-27 March, 3-5 June and 20-21 August various atmospheric gas sampling data were collected at ARKY and NOP sites. Regarding the several gases selected for study (H_2O , HDO, N_2O , CH_4/THC , CO_2 and O_3) partial deficiencies in data collection were experienced for methane, THC and HDO. Malfunctions of H_2O and O_3 sensors resulted in a partial loss of data collection for these gases as well. Data acquisition system malfunctions impacted collection of information for all gases during a few days of the planned measurement period, however supplemental runs were performed during the period 6-10 June to replace missing data.

Water vapor measurements were variable showing diurnal variations on some but not all days. Values observed at ARKY site during March and June varied between a low value of 1.5 torr and a highest value of 6 torr. Measurements at NOP site collected during 10-28 April show greater fluctuations and less diurnal variation than the ARKY site data and appear to be influenced to a greater degree by changes in air mass. The range of values observed was comparable to the ARKY data -- approximately 1.7 torr to 6.9 torr.

The N_2O measurements collected at ARKY show a nearly constant value of ~ 0.34 ppm on 3 and 4 June with a decrease to 0.28 ppm on 6 June which persisted until the end of the measurement period on 10 June. No tendency toward diurnal variations could be observed in the ARKY data but such was apparent in the data collected at NOP site. Here a range

of values between 0.26 and 0.39 ppm was observed with an average value of 0.31 ppm.

Only sparse data on CH_4/THC concentrations were obtained at either site due to the variety of equipment malfunctions described in Sections 2.2 and 2.3. Low values were monitored at each site (<1.4 ppm THC at ARKY on 4 and 5 June and <1.2 THC at NOP on 22-24 April) with no apparent diurnal pattern.

Some diurnal variation was seen in the ozone data collected at ARKY site. Low values <15 ppb were observed in the early morning and higher values around 40 ppb occurred in the afternoon. The NOP site O_3 data showed comparable variations in magnitude but unlike the ARKY data no reproducible diurnal variations were seen.

Carbon dioxide concentrations measured at ARKY varied between 287 - 352 ppm and did not exhibit a diurnal pattern of change while data collected at NOP site showed a diurnal change with a maximum value of around 390 ppm occurring in the morning around 0700 and a minimum value of about 340 ppm in the evening near 1700 hours. The average value observed in the NOP data was about 360 ppm, about 20% larger than the corresponding average value of the ARKY site measurements.

Operational problems were encountered with both the MRI nephelometer and GCA aerosol mass monitors used to measure aerosol loading. Gain instability in the MRI instrument and zero drift encountered with the GCA monitor required frequent recalibration, resulting in significant loss of data during the measurement periods. The limit of measurement sensitivity of each device is taxed by the aerosol loading values encountered which were always less than $40 \mu\text{gm}/\text{m}^3$ and usually less than half that value.

Diurnal trends in concentration variations were observed for some of the gases being monitored but these

variations were not consistently reproducible from site to site nor for the same site on successive days. It would be advantageous to incorporate simultaneous measurements of insolation and wind speed and direction along with the gas concentration data being collected. This would facilitate association of diurnal or otherwise periodic variations in one or more of the gas concentrations being monitored with changes in air mass and/or changes in solar flux and attendant photosynthetic and respiration activity.

The large number of independent monitoring instruments and supporting subsystems used to simultaneously collect atmospheric concentration data on the several gases of interest reduces appreciably the likelihood that all measurements will be available and functioning satisfactorily during the required data collection periods. A substantial division of effort unavoidably occurs and difficult orchestration of the measurements results. Reduction of the number of independent measurement systems needed to fully characterize infrared atmospheric absorption should be emphasized as a long term goal.

It is important that useful statistical measures be developed from the gas concentration measurements for use as modeling parameters as soon as feasible. The large volume of data presented as plots in this and previous reports is rather intractable as it stands; ready assimilation of the important information contained in these data is impaired by the need to review large numbers of individual measurements. Summary statistics not only of individual gas concentration variations but also of composite molecular absorption coefficients based on them should be generated. Seasonal bounds and diurnal variations in these statistical measures should be developed. Processing of the data as it is collected into seasonal running

averages of maximum, mean and minimum values and probability of occurrence of these values should be undertaken. Extinction coefficients at the several HEL wavelengths of interest should be calculated in developing this statistical base.

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